Photoluminescence properties of coatings on A356 containing Al_2O_3, Sm_2O_3 and ZrO_2 synthesized by zol-gel technology

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Abstract: *Thin coatings of aluminum oxide (Al_2O_3), zirconium oxide (ZrO_2) and samarium oxide (Sm_2O_3) on aluminum alloy Al7SiMg (A356) were prepared by sol-gel method and immersion technique. The materials were characterized in detail by X-ray diffraction. The luminescent properties at room temperature were also investigated. Luminescence analysis showed that the Al_2O_3 coating containing ZrO_2 exhibits broad excitation and emission bands, peaking at 328 nm and 392 nm, respectively. Photoluminescence data for the Al_2O_3 coating containing ZrO_2 and Sm_2O_3 indicated effective excitation at 404 nm and strong broadband emission, which is due to the co-emission of ZrO_2 and Sm_2O_3. Chromaticity coordinate analysis revealed that Al_2O_3 coating containing ZrO_2 and Al_2O_3 coating containing ZrO_2 and Sm_2O_3 emit in the blue-purple and pale pink regions, respectively.The chromaticity coordinates, color purity and CIE (Commission Internationale de L'Eclairage) color-correlated temperature were determined.*

Keywords: A356, LUMINESCENCE, SOL GEL, COATINGS, Al_2O_3 ,, ZrO_2, Sm_2O_3

1. Introduction

The development of multifunctional coatings for light metal alloys has received considerable attention due to their potential applications in aerospace, automotive, and energy sectors. Aluminum alloys, especially the A356 alloy, are widely used because of their low density, good mechanical properties, and excellent castability. However, their relatively poor corrosion and wear resistance limit their long-term performance in aggressive environments [1].

In this article, the surface of a 70/70 current terminal coated by the sol-gel method is investigated. It is an assembly of two parts made of AlSi7Mg alloy, used in the power grid (Figure. 1).

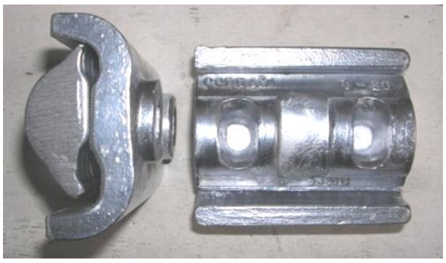

Figure 1.

Metal molds (tools) are used to obtain the castings. Before work, the tool is uses coverage [2,3,4] to obtain a good surface, orientate directional crystallization and provide good feeding of the casting. For the actual part of the casting, Wolfraco coating is used.

Sol-gel technology has emerged as a versatile and cost-effective method for the fabrication of oxide-based thin films and coatings on metallic substrates [5]. This method allows for low-temperature processing, compositional control, and homogeneous distribution of dopants at the molecular level [6, 7].

Luminescent properties of Sm^{3+} ions show sharp emission peaks around 560–650 nm when excited in the UV region. The intensity and profile of the emission bands are sensitive to the local environment, defect states, and thermal history /Figure 2/.

As it is well known, the luminescent properties of ZrO_2 appear to be highly influenced by the methods used for its preparation. For instance, tetragonal ZrO_2 nanoparticles produced via microwave irradiation exhibit emission peaks at 402, 420, and 459 nm when excited at 254 nm, and a broad band at 608 nm at 412 nm excitation. In contrast, colloidal zirconia nanocrystals synthesized through a two-phase process display a broad emission centered around 365 nm when exposed to 250 nm UV excitation. Therefore, exploring alternative methods to synthesize ZrO_2 would be both valuable and meaningful for investigating the luminescent properties.

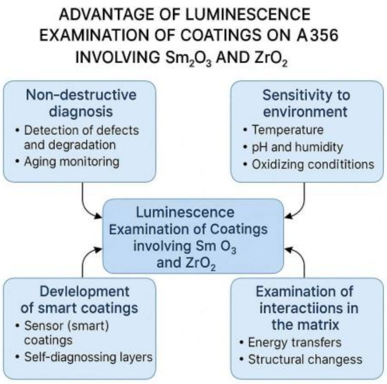

Figure 2.

In this work, we investigate the photoluminescence properties of Sm_2O_3 -Al_2O_3 doped–ZrO_2 coatings synthesized via sol-gel technique and deposited on A356 aluminum alloy. The influence of samarium concentration on the structural and optical characteristics of the coatings is systematically examined.

2. Experimental procedures

2.1. Materials

Commercially available A356 aluminum alloy castings (nominal composition: 7.0% Si, 0.3% Mg, balance Al) were used as substrates. The substrates were cut into rectangular shapes (20 × 10 × 5 mm^3), mechanically polished with silicon carbide paper to 1200 grit, degreased in ethanol and ultrasonically cleaned in deionized water.

The materials used for sol-gel synthesis included aluminum nitrate [$Al(NO_3)_3 .9H_2O$], zirconium oxychloride [$ZrOCl_2.8H_2O$] and samarium [Sm_2O_3], all obtained from AGC Glass Europe with a purity of >98%. 99.9% ethanol (C_2H_5OH) and nitric acid HNO_3 were used as solvents and stabilizing agents, respectively.

2.2. Sol Preparation

Two separate compositions were prepared based on the following compositions:

1. Al_2O_3 and ZrO_2 . 2. Al_2O_3 , ZrO_2 , and Sm_2O_3

The sol-gel solutions were prepared by hydrolytic condensation. Initially, aluminum nitrate was dissolved in deionized water and absolute ethanol under vigorous stirring at room temperature. Nitric acid was added dropwise to stabilize the solution and control the rate of hydrolysis. Separately, $ZrOCl_2.8H_2O$ was diluted in ethanol and added to the aluminum sol under continuous stirring. In the second composition involving Al_2O_3, ZrO_2, and Sm_2O_3 - nitric acid was added dropwise to the samarium oxide and introduced into the mixture containing Al_2O_3 and ZrO_2 to obtain the desired rare earth element content (0.5–2.0 mol%). The final two sols were stirred for 8 hours to ensure homogeneity and aged for 72 hours before coating.

2.3. Coating

The prepared sols were coated onto A356 substrates using the dip-coating technique at a draw speed of 5 cm/min. After deposition, the wet films were dried at 120°C for 1 hour to remove residual solvents. The coating process was repeated 1–3 times to achieve the desired thickness (~20 nm). The coated samples were subsequently heat-treated in air at temperatures of 420°C for 2 hours to promote densification and crystallization.

2.4. Characterization Techniques

Photoluminescence (PL) measurements were performed at room temperature using a fluorescence spectrometer (Horiba Jobin Yvon Fluorolog) with an excitation wavelength of 405 nm. Emission spectra were recorded in the range of 400–750 nm to evaluate the characteristic transitions of Sm^{3+} and Zr^{2+} ions.

3. Results and Discussion

Photoluminescence (PL) spectroscopy is essential for studying the optical characteristics of newly synthesized materials. Al_2O_3 does not possess luminescent properties. The PLE spectra of Al_2O_3 - ZrO_2 coating was recorded at room temperature by monitoring the most intensive characteristic emission of ZrO_2 ions at 392 nm wavelength, as shown in Figure 3.

Photoluminescence (PL) spectra

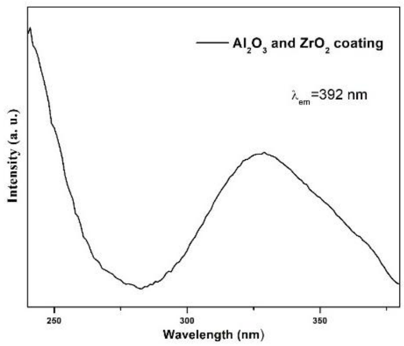

Figure 3. *Excitation spectrum of the Al_2O_3 - ZrO_2 coating*

The Figure 4 shows PLE spectrum containing two continuous strong broad bands with spanning wavelengths below 280 nm and from 280 nm to up to above 350 nm, with a prominent peak centered at 241 and 328 nm, respectively. The second peak was chosen for recording the emission spectrum.

Up to now, the origin of ZrO_2 luminescence is not clear and there are several different proposed mechanisms [8]. More precisely, since Zr^{4+} ions do not inherently exhibit luminescence, the emission observed in ZrO_2 is likely attributed to defects and/or impurities within the system, as has been noted in similar manuscripts [9, 10]

The luminescence characteristics of our Al_2O_3 - ZrO_2 coating, such as excitation and emission wavelengths positions, clearly differ from those reported for samples synthesized by other methods discussed in the Introduction section. Moreover, the excitation spectrum is shifted by about 10 nm and the emission spectrum by about 30 nm compared to our previous study on ZrO_2 coatings on glass. This effect may be due to the fact that in this case the coating is deposited on an aluminum alloy. This indicates that various synthesis techniques introduce distinct types of defects and/or impurities in ZrO_2, which significantly influence its luminescent behavior.

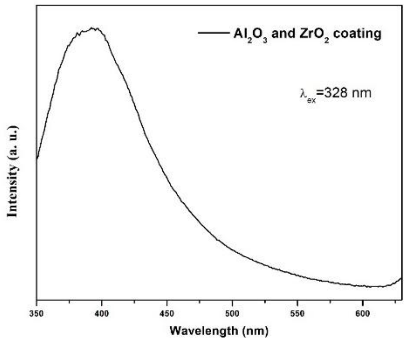

Figure 4. Emission spectrum of the Al_2O_3 - ZrO_2 coating

The photoluminescence behavior of ZrO_2 coating containing both Al_2O_3 and Sm_2O_3 was studied using the excitation wavelength of 404 nm and is shown in Figure 4. The obtained coating is characterized by strong broad band luminescence, which is due to the co-emission of ZrO_2 and Sm_2O_3. The emission peak at 468 nm corresponds to the ZrO_2 emission. The incorporation of Sm_2O_3 has resulted in the appearance of new emissions in the visible range, which are clearly observed as bands at about 534 nm, 600 nm and 688 nm due to its characteristic intra-configurational f-transition $^5G_{5/2}\rightarrow{}^7H_J$, where J = 5/2, 7/2 and 11/2, respectively [11,12].

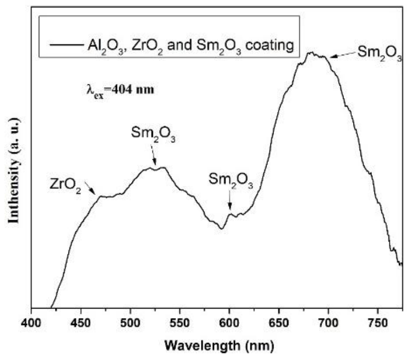

Figure 4. *Visible emission spectra of the Al_2O_3 - ZrO_2 - Sm_2O_3 coating*

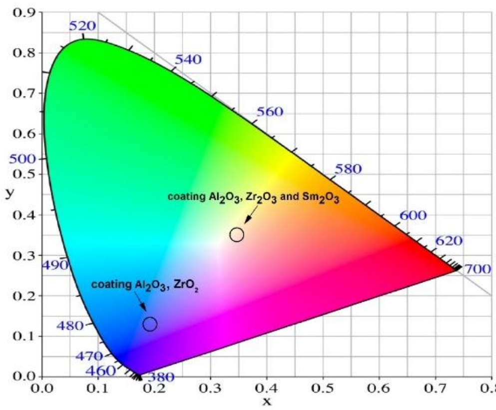

Figure 4. *CIE chromaticity diagram of Al_2O_3 - ZrO_2 and Al_2O_3 - ZrO_2 - Sm_2O_3 coatings*

To determine the precise emission colors, the CIE 1931 chromaticity diagram was used (Figure 4) [13]. The chromaticity coordinates were calculated from the emission spectra using the SpectraChroma software (Version 1.0.1), a CIE coordinate calculator [14]. The obtained values for Al_2O_3 - ZrO_2 coating are 0.19:0.142 and correspond to blue-purple color of emission, while for Al_2O_3 - ZrO_2 - Sm_2O_3 coating are 0.344:0.363 corresponding to pale pink color.

The correlated color temperature (CCT) was determined using McCamy's empirical formula:

$$CCT = -449n^3 + 3525n^2 - 6823n + 5520.33$$ [15]

where $n= (x-x_e)/(y-y_e)$ is the reciprocal slope, (x_e=0.332, y_e=0.186) are epicenter of convergence and x and y are the chromaticity coordinates.

Phosphors with CCT values under 3200 K are typically classified as warm light sources, whereas those exceeding 4000 K are regarded as cool light sources. The Al_2O_3 - ZrO_2 coating has a calculated CCT of 6263.08 and for Al_2O_3 - ZrO_2 - Sm_2O_3 coating is 5086.43 indicating that they function as cold light-emitting materials.

4.Conclusion:

In conclusion, innovative Al_2O_3 - ZrO_2 coating and Al_2O_3 - ZrO_2 - Sm_2O_3 coating were successfully fabricated on aluminum alloy castings using the sol-gel method combined with dip coating.

Luminescence analysis showed that the Al_2O_3 - ZrO_2 coating exhibits broad excitation and emission bands, peaking at 328 nm and 392 nm, respectively. Photoluminescence data for the Al_2O_3 - ZrO_2 - Sm_2O_3 coating indicated effective excitation at 404 nm and strong broadband emission, which is due to the co-emission of ZrO_2 and Sm_2O_3. Chromaticity coordinate analysis revealed that Al_2O_3 - ZrO_2 and Al_2O_3 - ZrO_2 - Sm_2O_3 coatings emit in the blue-purple and pale pink regions, respectively.

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